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Synthesis and electroplating of high resolution insulated carbon nanotube scanning probes for imaging in liquid solutions

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Abstract

High resolution and isolated scanning probe microscopy (SPM) is in demand for continued development of energy storage and conversion systems involving chemical reactions at the nanoscale as well as an improved understanding of biological systems. Carbon nanotubes (CNTs) have large aspect ratios and, if leveraged properly, can be used to develop high resolution SPM probes. Isolation of SPM probes can be achieved by deposited a dielectric film and selectively etching at the apex of the probe. In this paper the fabrication of a high resolution and isolated SPM tip is demonstrated using electron beam induced etching of a dielectric film deposited onto an SPM tip with an attached CNT at the apex.

Introduction

Energy storage and conversion are necessary components for mobile electronic devices and green technologies. Continued development of these technologies as well as others have hinged on the availability of portable power sources combining high-energy density batteries with long cyclic lifetimes. [1] One limiting factor in the current design of batteries and fuel cells is the lack of understanding of the microscopic mechanisms of their operation at the nanoscale. Recently, a number of scanning probe microscopy techniques [2] including Kelvin Probe Force Microscopy (KPFM) have been applied for probing ionic and transport phenomena in energy materials. Novel techniques such as electrochemical strain microscopy (ESM) have been developed for probing ionic processes in solid [3–5]. However, implementation of KPFM, ESM and related techniques in liquid electrolyte environments necessitates the development of high aspect ratio isolated SPM probes that can essentially act as nanoelectrodes.

Similar need for insulated SPM probes emerges in the context of electrochemical and electromechanical probing of biological systems[6–8]. Here, SPM measurements must be performed in a liquid to keep the system biologically viable and mimic the environment of cells and biomolecules [9–11]. An advantage of the measurements being made in solution is the improved control over the probe-surface forces and minimization of the competing capillary interactions. Similarly to electrochemical systems, to enable the measurements in solution the tip must be insulated everywhere except at the apex in order to eliminate the stray electronic and ionic currents through the liquid electrolytes and associated heating of solution and stray electrochemical reactions [12–14].

Concurrent to the electrical and electrochemical measurements in solution there is a demand for high spatial resolution. The latter necessitates reduced interaction region of the apex of

the tip. And ideally higher aspect ratio of the conical part of the probe [14]. One method for the size reduction or increased aspect ratio is to attach a high aspect ratio material, such as carbon nanotube (CNT) or nanowire, at the probe apex [15]. In this paper, we demonstrate a synthesis route for an electrically shielded carbon nanotube scanning probe tip offering high resolution and electrical isolation.

Standard Insulated Scanning Probes

Illustrated in Figure 1 is a sequence of scanning electron microscopy (SEM) images demonstrating the steps involved in synthesizing an insulated (covered by insulator) or shielded (having additional external shield) scanning probe tip. Figure 1a shows the as-received silicon scanning probe and 1b shows the tip after a 30 nm Pt conductive layer and etch stop layer was deposited (albeit thinner at the tip due to geometric considerations of the nearly line-of-site deposition). The platinum sputtering conditions were 10 W dc power (150mm diameter target), 3 mTorr pressure and an approximate source to substrate distance of 7.5 cm. Figure 1c is the tip after a 50 nm thick silicon nitride film was deposited (process conditions given below) and Figure 1d is the tip after a selective focused electron beam induced etching at the tip apex. For more information on electron beam induced processing (EBIP) see refs. [16–18]. In addition to the listed reviews of EBIP, recent work by Lobo et al. [19] demonstrated sub-1 nm length scales with a combined electron beam induced etch (EBIE) and deposition (EBID) process via simulations.

The high uniformity of dielectric coating can be demonstrated by electroplating experiment illustrated in Figure 1e. Here, the shielded SPM tip mounted in an Asylum Research MFP-3D AFM platform and is then submerged in a droplet of gold electroplating solution (Orotherm HT) on a gold substrate. A -1 V bias is applied and gold is deposited onto the conductive paths of the SPM tip from the gold solution. Using a 1.5 M-ohm resistor in series with the AFM tip a variable current was measured during the 10-minute deposition (see figure 1g). The estimated volume deposited at the apex ($0.11 \mu\text{m}^3$) is comparable with the calculated gold volume deposited ($1.2 \mu\text{m}^3$, assuming 100% efficient deposition) [overall efficiency of ~10%]. The decrease in current with time during the electrochemical deposition is due to ion depletion in the solution, which could also contribute to the difference between calculated gold volume and the volume of the deposit at the AFM tip. No Au deposition on other parts of the probe was observed during SEM imaging, illustrating the high quality of the dielectric coating.

SiN_x Deposition

Carbon nanotube based scanning probes were received from Xidex Inc. The first step in the CNT shielded probe synthesis was to deposit a 50 nm thick SiN_x film onto the AFM tip with a single attached CNT at the apex. A Si rich plasma enhanced chemical vapor deposition (PECVD) recipe was an obvious choice for the dielectric coating since it minimizes the stress when deposited onto the cantilever. The Si rich PECVD recipe was performed in an Oxford Instruments PlasmaLab System 100 at 40 W RF power, 350°C and 600 mTorr with a 5%SiH₄/Ar gas flow of 150 sccm, NH₃ flow of 2 sccm and a N₂ flow of 790 sccm. The deposition rate of this recipe was measured at 0.22 nm/s for a 10-minute deposition following the 5-minute chamber-seasoning step thus a deposition time of 3-minutes and 47-seconds was used with a portion of the SPM sample covered for electrical contact.

SiN_x Etching

The next step of the insulated CNT-scanning probe synthesis was to etch the SiN_x covering the CNT. Selective nanoscale etching was performed in an FEI Nova 600 scanning SEM/FIB (focused ion beam) system using EBIE with a XeF₂ precursor gas [20–24]. The gas injection

nozzle ($\sim 250\mu\text{m}$ inner diameter) was inserted $\sim 200\mu\text{m}$ from the sample surface and the system pressure during etch was $\sim 3\times 10^{-6}$ Torr and based on [25] we estimated a localized flux of XeF_2 of $\sim 8\times 10^{17}\text{ XeF}_2/\text{cm}^2$ (assuming a gas spread angle of 30 degrees). In addition to the XeF_2 precursor, Roediger et al. [26, 27] and Vanhove et al. [28] have also demonstrated EBIE of Si with Cl and SF_6 chemistries, respectively. EBIE can also be performed on non-Si based materials. Goler et al. [29] demonstrated etching of graphene nanostructures, Roediger et al. [30] has demonstrated removal of Ge, Schoenaker et al. [31] has etched Ti and Ganczarczyk et al. [32] has etched GaAs to list a few recent discoveries. To perform this step, various parameters were investigated on test SiN_x samples including: variable electron beam energy and current, as well as the pump-down time in the chamber (water concentration and residual carbonaceous gases). We observed the electron beam induced etching rates of the SiN_x were dependent on the beam current density, electron-beam working distance (precursor flux), dwell time, refresh time and chamber pressure which have all been previously reported [21–24, 33]. Ultimately good etch selectivity was achieved for the electron beam induced etching of the SiN_x versus the carbon nanotube. Figure 2 shows the post-etch diameter of a SiN_x coated CNT as a function of the number of passes of the etch process. These results show a dependence on the diameter of the CNT. This diameter dependence is a result of additional volume of SiN_x due to the increased initial surface area and the conformal SiN_x coverage and growth. The lower etch rate of the larger CNTs could also be related to increased charging leading to drift. Drifting would result in a reduced dwell time per area there therefore a reduced local etch. Additionally, the inset of Figure 2 (a and b) show a SiN_x coated CNT that was etched. In Figure 2a the SiN_x was completely removed after 100k passes. In Figure 2b 500k passes were performed with no additional etching. This high selectivity between the SiN_x and the CNT is desired for this work. When applying this processing step to the isolated CNT SPM tip etching of the SiN_x without damage or etching to the CNT is required. In each of the example etches shown here a 5 keV and 400 pA scanning electron beam with XeF_2 locally injected at the substrate surface (1×10^{-6} Torr background pressure) was used with a 1 μs dwell time and a 100 μs refresh time. These samples were pumped-down for 2 hours prior to etching to remove additional water in the chamber and reduce the pressure.

Extensive etch testing revealed that the CNT etch rates depended significantly on an O_2 plasma chamber clean and the pump-down time. When the O_2 plasma chamber clean was performed water is introduced into the chamber. At short pump-down times water remains in the chamber and is slowly pumped out at longer pumpdown times. Previous work by Yuzvinsky et al. [34] demonstrated that electron-beam induced etching of CNTs is enhanced with the injection of water vapor. While specific partial pressure information is not known because the system does not have a residual gas analyzer, when the chamber was allowed to pump down for a minimum of 2 hours after the O_2 plasma clean, no CNT etching was observed.

Figure 3 shows the effects of the plasma cleaning time on the CNT etching (with a localized H_2O partial pressure of $\sim 1\times 10^{-4}$ Torr estimated by Kohlmann et al. [25] and the background pressure of $\sim 5\times 10^{-6}$ Torr) where the competitive carbon deposition is obvious from the dark staining at the low plasma cleaning times. When a plasma clean is performed we were able to etch CNTs and the etch rate in the water ambient in general increases with increasing current and decreasing beam energy.

The previous results lead us to perform additional studies where we investigated how the time in the chamber (vacuum) changed the etch rates of both the SiN_x and the CNTs. Shorter pumpdown times lower the etch rate of the SiN_x , and the presence of water in the chamber promotes CNT etching (figure 3) with the electron-beam. Figure 4 shows the etch results of a SiN_x coated CNT as a function of increasing pumpdown time which illustrates the faster

etch rate with increasing pumpdown time which coupled with the fact that the CNT etch rate is accelerated by water improves the overall etch selectivity of the process. The inset of Figure 4 demonstrates the different etch rates for a 40-minute and 100-minute pumpdown time for the same SiN_x coated CNT. For the remaining experiments a minimum of 2 hours of pumpdown time was allowed prior to the etching process.

Tip Fabrication

As mentioned, the CNT-SPM tips were received from Xidex Inc., which are fabricated either by a pick-and-place process or via a direct CVD process. Subsequent to imaging the as-received CNT SPM tips, a SiN_x film was conformally deposited on the tip using the silicon rich silicon nitride recipe. The SiN_x layer was then etched at the tip to expose the CNT producing a small conductive region only at the tip. Figure 5a and 5b shows SEM images of the as-received SPM tip used in this work from a (a) top down view and a (b) 45 degree tilted view. The tip diameter is estimated to be 19 nm in diameter.

The PECVD growth of the Si rich SiN_x deposition was run for a target thickness of 40 nm. Figure 5 shows SEM images of the SPM tip with the SiN_x film from a (c) top down view and a (d) 45 degree tilted view. The film thickness of the SiN_x was measured with an ellipsometer on an accompanying silicon sample and was determined to be 53.25 nm thick. Comparing the diameter of the tip post-SiN_x deposition (~ 120 nm) confirmed that the deposition rate at the tip is consistent with the planar substrate.

The SiN_x was then etched using the EBIE process at the tip only to expose the CNT allowing a conductive path only at the CNT. The beam energy and current were 5 keV and 400 pA with a beam dwell time of 1 μs, a refresh time of 5 times the pattern loop time, an area overlap of 50%, a beam working distance of 4.0 mm and a total of 200k passes; where 50k passes were performed at angles of rotation of 0, 90, 180 and 270 degrees, respectively, around the AFM tip all at a tilt angle of 45 degrees. The rotation of the AFM tip for etching was performed to ensure uniform etching of the SiN_x around the CNT. Figure 5 shows SEM images of the AFM tip with attached CNT after the SiN_x was etched from the CNT. Prior to EBIE a base pressure of less than 1×10^{-6} Torr was achieved during a two-hour pumpdown time. During EBIE the flow of the XeF₂ caused a local rise in pressure to approximately 3×10^{-6} Torr. This pressure rise due to the flow of the precursor gas gives an estimate precursor flux of 8×10^{17} XeF₂/cm².

To confirm the electrical isolation of the shielded CNT probe, electrochemical testing by selective electrochemical deposition was also performed similar to what was demonstrated in figure 1 for the standard tips. Figure 5i shows the current measured during the electrochemical deposition. In this case a 30 M-ohm resistor was used in parallel with the tip. Similar to Figure 1g we see the same signature of an electrochemical deposition process when the tip is inserted into the solution, however the current quickly decreases back to the original current measured prior to inserting the tip into the solution. The observed current density of 5.5×10^9 A/m² is lower than some reported critical current densities associated with Joule heating induced multiwall carbon nanotube failure ($\sim 10^{13}$ A/m²) [35, 36], however, we opine that the PECVD silicon dioxide growth process could have damaged part of the CNT making it more susceptible to failure. However, as demonstrated in the image, there is no selective deposition around the nanotube and apex region which confirms that the probe is electrical isolated and that the brief current flow is restricted to the CNT. Future work will explore lower current compliance for localized electrochemical deposition as well as determining the scanning probe properties of the isolated CNT scanning probe tips as initial attempts were unsuccessful as the CNT tips broke when the tip was engaged on the surface.

Conclusions

An isolated, high-resolution scanning probe was fabricated using a CNT mounted at the tip apex. The electrical isolation was accomplished by coating a thin insulating layer and selectively and nanoscopically etching the insulating layer to partially expose the CNT using a focused electron beam induced etching process. The fabrication process requires achieving the proper chamber conditions to etch the SiN_x layer and leave the CNT behind. Based on our preliminary probe testing, slightly larger tip diameters need to be used for these applications to make them mechanically more robust.

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Figure 1.

SEM images of the process steps of the standard conductive AFM tip. (a) As-received standard conductive AFM tip. (b) 30 nm Pt sputtered onto AFM tip. (c) 50 nm SiN_x PECVD. (d) Electron beam induced etch with XeF₂. (e) Electrochemical deposition of Au. (f) Schematic of the setup for electroplating of the isolated AFM tip. (g) Current measurement during electrochemical deposition. The deposition begins at the location labeled start and ends at the location labeled end.

Figure 2.

Etch progress of SiN_x coated CNTs of different diameters as a function of the number of passes. The inset shows two etches with a different number of passes - (a) 100k passes and (b) 500k passes - where the CNT is not etched with continued etching.

Figure 3.

SEM images of different O₂ plasma clean and CNT etch processing times. a) 0 minute clean, 38 nm deposit of carbon from 120 seconds of process time. b) 0 minute clean, 35 nm deposit of carbon from 120 seconds of process time. c) 1 minute clean, 15 nm deposit of carbon from 120 seconds of process time. d) 2 minute clean, 17 nm etch with 90 seconds of process time. e) 4 minute clean, 17 nm etch with 46 seconds of process time.

Figure 4.

Plot of the final CNT + SiNx diameter from the same etch repeated over time from reaching vacuum to 100 minutes in 20 minute increments.

Figure 5. SEM images of the AFM tip with attached CNT at the apex. (a, b) as-received tip. (c, d) SiN_x coated tip. (e, f) isolated tip after SiN_x etch at tip apex. (g, h) isolated tip after attempted Au electrochemical deposition. (i) current measurement during electrochemical deposition.